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MASS SPECTROMETRY OF AEROSOLS FROM BOREAL
FORESTS AND WOOD COMBUSTION

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Academic dissertation

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Abbreviations

AMS	Aerosol Mass Spectrometer, Aerosol Mass Spectrometry
AN	Ammonium Nitrate
AS	Ammonium Sulfate
ASL	Above Sea Level
BBOA	Biomass Burning Organic Aerosol
BC	Black Carbon
CCN	Cloud Condensation Nuclei
CDP	Cloud Droplet Probe
CE	Collection Efficiency
COA	Cooking Organic Aerosol
CPC	Condensation Particle Counter
DMPS	Differential Mobility Particle Sizer
EC	Elemental Carbon
FTIR	Fourier Transform Infrared Spectroscopy
HOA	Hydrocarbon-like Organic Aerosol
HR	High Resolution
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory
IE	Ionization Efficiency
INT	cloud interstitial particles
LV-OOA	Low-Volatile Oxygenated Organic Aerosol
NIA	Nitrate Inorganic Aerosol
NPF	New Particle Formation
ON	Organic Nitrates
PAH	Polycyclic Aromatic Hydrocarbon
PM	Particulate Matter
PMF	Positive Matrix Factorization
RES	cloud droplet residual particles
RH	Relative Humidity
RIE	Relative Ionization Efficiency

SMEAR	Station for Measuring Forest Ecosystem-Aerosol Relations
SOA	Secondary Organic Aerosol
SP	Soot Particle
SV-OOA	Semi-Volatile Oxygenated Organic Aerosol
TOF	Time-of-Flight
TOT	total cloud particles
UMR	Unit Mass Resolution
VOC	Volatile Organic Compound

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Mass spectrometry of aerosols from boreal forests and wood combustion

Aki-Matti Henrik Kortelainen

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Abstract

Atmospheric aerosol particles, in addition to health effects, have a direct effect on climate change by scattering and absorbing solar radiation and an indirect effect by forming cloud condensation nuclei. Organic aerosols play a crucial role among the submicron aerosol mass at the northern hemisphere. The understanding of organic aerosol sources is a key issue for assessing their atmospheric influence and their biogenic and anthropogenic precursors. This thesis introduces organic aerosol sources from the biogenic-anthropogenic interactions in a boreal forest area and a new analysis approach to track particulate organic nitrates, the effect of cloud processing on organic-rich aerosol, and organic aerosol sources from combustion emissions.

A High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) was used to measure aerosol chemical composition in a remote boreal forest area, a boreal forestland-urban mixed region, and in laboratory experiments concentrated on the characterization of combustion emissions. Particulate organic aerosol was classified using the positive matrix factorization analysis method, integrating organics and nitrate ions for the first time to study their sources in two ambient locations. Furthermore, Organic aerosol sources were studied in detail from direct wood combustion emissions under different conditions.

Organic aerosol sources at both ambient sites were divided into SV-OOA (Semi-Volatile – Oxygenated Organic Aerosol and LV-OOA (Low-Volatile - OOA); the former represents less aged, local, mainly biogenic, aerosol sources while the latter denotes long-range transported aerosol. Anthropogenic activities such as traffic and industrial emissions in the vicinity produced HOA (Hydrocarbon-like OA) at the boreal forestland-urban mixed site, representing fresh primary organic aerosol. Regarding cloud processing, HOA and SV-OOA were higher in cloud interstitial particles while LV-OOA was higher in cloud residual particles due to longer aging time. In boreal forest setting, particulate organic nitrates were formed by the nocturnal chemical reactions between anthropogenic emissions (which produced the nitrate radical) and forest emissions (which produced Biogenic Volatile Organic Compounds (BVOCs)). Organic aerosol from direct wood combustion emissions had characteristics similar to ambient air factors of HOA, LV-OOA, BBOA (Biomass Burning-OA). We also identified new factors of PAHs (Polycyclic Aromatic Hydrocarbons) and Aromatics; the former formed during smoldering combustion conditions caused by the momentarily decreased combustion efficiency.

From the anthropogenic-biogenic interactions in the boreal forest area, the organic factors established well the organic aerosol sources. The factors characterized in high resolution were in good agreement with those in previous studies at the same boreal forest site and similar locations. According the results from novel PMF analysis based method only a small fraction of particles consists of organic nitrates in boreal forest areas, being a feature of such relatively clean air regions. The new method utilized the organic nitrate functional group while previous studies used the peroxy radical. Cloud processing seemingly increased the aged low-volatile form of organic aerosol, consistent with the long aging time in the air. The new HR PAH factor in combustion studies provided new information from particulate PAHs, representing their time-dependent behavior in rapidly changing conditions. This work introduces a detailed analysis of particulate organic aerosol under various circumstances; this analysis could prove useful in work on aerosol mass spectrometry.

Keywords: organics, organic nitrates, aerosol chemical composition, aerosol mass spectrometry

Contents

1	Introduction	10
2	Overview of atmospheric aerosols	12
2.1	Aerosol sources	12
2.1.1	Biogenic sources	12
2.1.2	Anthropogenic sources	13
2.2	The composition of atmospheric aerosols	14
2.2.1	Inorganic compounds	14
2.2.2	Organic compounds	15
2.2.3	Refractory compounds	16
3	Materials and methods	17
3.1	High resolution time-of-flight aerosol mass spectrometer	17
3.1.1	Operation	17
3.2	Measurements	20
3.2.1	Field measurements on SMEAR II site	21
3.2.2	Field measurements on SMEAR IV site	21
3.2.3	Laboratory experiments	22
4	Results	24
4.1	Chemical composition of submicron aerosol particles in the boreal forest area ...	24
4.1.1	Biogenic and anthropogenic organic aerosol sources	24
4.1.2	Organic nitrates	27
4.2	Direct combustion emissions	29
4.2.1	Combustion phases	29
4.2.2	Aerosol sources	30
5	Review of papers and the author's contribution	32
6	Conclusions	34
	References	36

List of publications

This thesis is based on data presented in the following articles, referred to by the Roman numerals I–IV. The publications have been included at the end of this thesis with their copyright holders' permission.

- I Kortelainen, A., Joutsensaari, J., Hao, L., Leskinen, J., Tiitta, P., Jaatinen, A., Miettinen, P., Sippula, O., Torvela, T., Tissari, J., Jokiniemi, J., Worsnop, D. R., Smith, J. N., Laaksonen, A. and Virtanen, A., Real-time chemical composition analysis of particulate emissions from woodchip combustion, *Energy& Fuels*, 29(2): 1143-1150, 2015.
- II Kortelainen, A., Hao, L., Tiitta, P., Jaatinen, A., Miettinen, P., Kulmala, M., Laaksonen, A., Smith, J. N., Worsnop, D. R. and Virtanen, A., Sources of particulate organic nitrates over the boreal forest in Finland, submitted in *Boreal Environment Research* 15.3.2016.
- III Hao, L., Kortelainen, A., Romakkaniemi, S., Portin, H., Jaatinen, A., Leskinen, A., Komppula, M., Miettinen, P., Sueper, D., Pajunoja, A., Smith, J. N., Lehtinen, K. E. J., Worsnop, D. R., and Laaksonen, A. and Virtanen, A., Atmospheric submicron aerosol composition and particulate organic nitrate formation in a boreal forestland-urban mixed region, *Atmospheric Chemistry and Physics*, 14, 13483-13495, 2014.
- IV Hao, L., Romakkaniemi, S., Kortelainen, A., Jaatinen, A., Portin, H., Miettinen, P., Komppula, M., Leskinen, A., Virtanen, A., Smith, J. N., Sueper, D., Worsnop, D. R., Lehtinen, K. E. J. and Laaksonen, A., Aerosol chemical composition in cloud events by high resolution time-of-flight aerosol mass spectrometry, *Environmental Science and Technology*, 47(6): 2645-2653, 2013.

1 Introduction

Atmospheric aerosols have many sources; their formation and chemical composition are complex. Ambient aerosols consist of liquid, solid and semi-solid particles from sizes ranging from a few nanometers to tens of micrometers (the diameter of human hair) and surrounding gas (Seinfeld and Pandis, 2006). Knowledge of particle formation has recently increased with the development of measurement methods and modelling simulations. So-called new particle formation (NPF) events have continually been observed worldwide, and their precursors have been one of the main focuses of recent atmospheric research (Kulmala, 2003; Kulmala et al., 2004). To understand the climate effects of aerosols, a better understanding on formation and chemical and physical properties of aerosol particles is necessary.

Atmospheric aerosols have a remarkable effect on human health and climate. The direct effect on climate is from aerosol scatter and the absorption of solar radiation. The indirect effect is that aerosol particles can form cloud condensation nuclei (CCN) (IPCC, 2013) (See Fig. 1). CCN activation to cloud droplets depends on the chemical composition and adequate water vapor supersaturation. High number concentrations of cloud droplets may decrease their mean size, making clouds optically thicker; this decrease, in turn, may delay precipitation and increase the lifetime of clouds (Twoney et al., 1974; Albrecht et al., 1989; Komppula et al., 2005). In Europe, currently, aerosol particle concentrations lead to more than 400 000 premature annual deaths, increased hospital admission, and restricted activity in tens of millions of children and people suffering from chronic cardiovascular and pulmonary disease (WHO 2003; EEA 2014).

The chemical composition of aerosol sources depends on natural and human activities. Particles can originate directly from emission sources such as industry, traffic, biomass burning, seas and deserts (Primary particles). They can also be formed via chemical reactions of gaseous compounds such as the oxidation of volatile organic compounds (VOCs) (Secondary particles) (Kulmala, 2003). In the atmosphere, secondary particles form by nucleation, which is a first step of gas-to-particle conversion where liquid or solid nucleus form from supersaturated vapor. In homogeneous nucleation particles form directly from the condensing air with low saturation vapor pressure and in heterogeneous nucleation new phase is formed onto existing surface. Atmospheric particles grow by condensation, where vapors condense onto the particles, increasing particle mean size. Important parameters for condensing compounds are surrounding temperature and low saturation vapor pressure of compounds. Opposite mechanism that decrease particle mean size is evaporation. Other particle growth mechanisms are coagulation, where particles merge due to collisions and agglomeration, where particles collide and stuck forming bigger irregular shaped particles, agglomerates. Particles are removed from the atmosphere via wet or dry deposition (See Fig. 1). Wet deposition occurs as water droplets are removed from the atmosphere by rain-out.

Multiple organic compounds from various sources play a crucial role in gas and particle chemistry in the atmosphere. Globally, organic aerosol particles constitute 20-90% of sub-micron aerosol mass (Jimenez et al., 2009). In Finnish boreal forest areas, organic mass covers 61% of the submicron aerosol (Raatikainen et al., 2010). In combustion emissions from masonry heaters, the organic content of fine particle emissions is 31-78% (Tissari et

al., 2007). In addition, organic content of traffic related submicron aerosol particles covers 41-54 % at highway and roadside environments (Enroth et al., 2016). As the organic content of submicron aerosol particles is generally high in the atmosphere, this study focuses on the chemical characterization of complex organic aerosol particles.

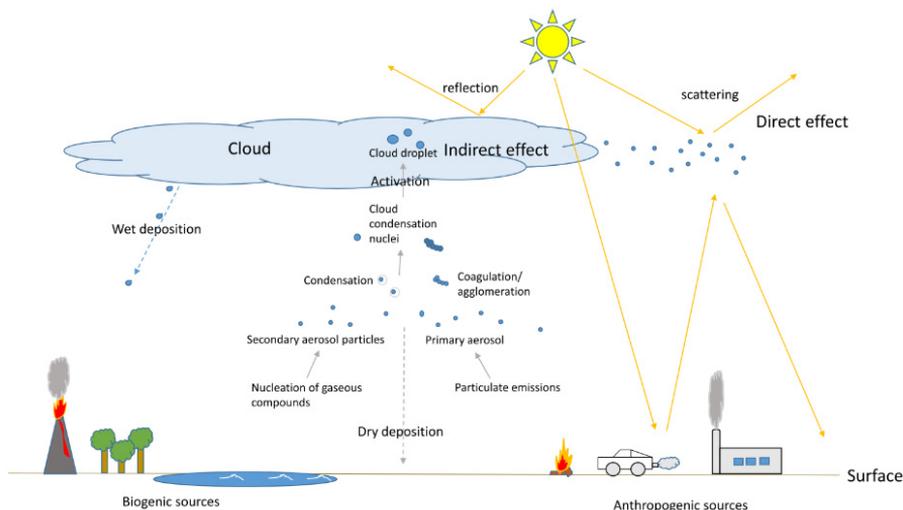


Figure 1: Atmospheric effects of aerosol

Methods for the chemical composition measurements of particles may be offline (i.e. filter sampling) or online (direct measurements). In addition, indirect methods for chemical composition analysis focus on measuring aerosol particle properties such as hygroscopicity and volatility (Rader and McMurry, 1986; McMurry, 1996). The present study concentrates on aerosol mass spectrometer (AMS) measurements, which detect the real-time chemical composition of submicron aerosol particles (Jayne et al., 2000, Jimenez et al., 2003). AMS allows fast time resolution and size-segregated analysis that offline methods cannot perform and yields direct information from atmospherically most chemical compounds, especially organics, at submicron size range. In addition, using mathematical positive matrix factorization (PMF) analysis on AMS data enables the classification of organic and inorganic sources and the identification of their properties in the atmosphere in detail (Ulbrich, 2009).

The emphasis of this study was to use AMS measurement method and specially, PMF based methods, in different measurement environments and under different circumstances to investigate atmospherically relevant research questions identified below. The direct wood combustion emissions chemical composition was characterized for the first time with PMF method. In the case of ambient aerosol particles, we concentrated to study the chemical composition of particles from anthropogenic-biogenic origin and the evolution of the chemical composition due to the cloud processing. The main research objectives were 1) to examine sources of organic aerosol particles in a boreal forest environment (paper II) and a boreal forestland-urban mixed region (paper III), 2) by measuring organic nitrates (papers II and III), to investigate anthropogenic-biogenic interactions 3) to assess how cloud processing affects the composition of organic-rich aerosol particles (paper IV) and 4) to study the formation of organics, particularly PAHs, in combustion (paper I).

2 Overview of atmospheric aerosols

2.1 Aerosol sources

Atmospheric aerosol particles, based on their formation methods, can be divided into primary and secondary aerosol. The particles result from anthropogenic, human activities, and biogenic, natural activities (Seinfeld and Pandis, 2006). While sources directly emit primary aerosol particles, secondary aerosol particles form by nucleation in the gas phase of subsequent condensable vapors. The accumulation (0.1-2 μm) and coarse (2-50 μm) modes dominate mass and volume distribution of atmospheric aerosol particles. The number distribution of aerosol particles, on the other hand, is dominated by nucleation (below 10 nm) and the Aitken mode (10-100 nm). Accumulation mode particles are from primary emissions, the condensation of secondary gas phase species, and the coagulation of smaller particles. Nucleation mode-sized particles are usually fresh secondary aerosol originating from NPF events. Aitken mode particles are typically primary aerosol particles, onto which secondary matter condenses in the atmosphere. Particles in the coarse mode are mainly related to primary aerosol particles originating from the mechanical processes of wind and erosion as well as brake wear and road-tyre interaction. The present work focuses on particle sizes ranging from the Aitken mode to the lower accumulation mode.

Atmospheric secondary aerosol particles form by nucleation and condensation. The vapor pressure of condensing gases should be low enough that they can nucleate or condense in low atmospheric concentrations. This process is often regulated by chemical reactions. With low vapor pressure, the most relevant compounds in atmospheric nucleation are sulfuric acid, amines and oxidized hydrocarbons (Kulmala et al., 2000; Marti et al., 1997; O'Down et al., 2002; Almeida et al., 2013; Riccobono et al., 2014). Organic compounds have a crucial role in particle growth to CCN sizes. Particles growth is described by growth rate that can vary according to surrounding circumstances and reach values of 1 to 20 nm hour⁻¹ (Kulmala, 2003). Fine particle lifetimes can vary from days to weeks, during which they transport in the atmosphere 1 km in a 100-1000 s (Seinfeld and Pandis, 2006).

2.1.1 Biogenic sources

Typical biogenic primary aerosol sources are seas (sea salt), lakes, deserts (dust), forests, vegetation (pollen, mold, spores) and animals (debris) (Seinfeld and Pandis, 2006). Biogenic secondary organic aerosol (BSOA) particles are formed by the gas-phase oxidation of biogenic volatile organic compounds (BVOCs) originating from vegetation. BVOCs cover 90% of total VOC emissions, playing a key role in a global SOA budget (Guenther et al., 1995; Tsigaridis et al., 2003; Hallquist et al., 2009). The composition and emission strength of BVOCs depend on vegetation types, seasons, temperature, solar radiation and precipitation (Guenther et al., 1993; Kesselmeier, J. and Staudt, M., 1999; Kuhn et al., 2004; Mochizuki et al., 2015). In Finnish boreal forest areas, BVOCs consist mainly of monoterpenes (α -pinene, β -pinene, camphene, ³ Δ -carene, sabinene, 1,8-cineol) (Hakola et al., 2009). Overall, BVOCs of isoprene, monoterpenes and sesquiterpenes are highly reactive (Chan et al., 2015).

BSOA particles formation depends on BVOC reaction with the atmospheric oxidants: the OH radical, ozone (O₃) and the nitrate radical (NO₃) with or without photolysis. The relative importance of the reactions depends on the molecular structure of the VOC and ambient conditions (Atkinson and Arey, 2003). The initial oxidation step generates a set of organic products containing one or more polar oxygenated functional groups such as aldehyde, ketone, alcohol, nitrate, peroxyacyl nitrate and carboxylic acid, all of which lead to less volatile and more water-soluble products (Hallquist et al., 2009). The oxidation of VOCs by OH starts with the abstraction of a hydrogen atom or addition to a C=C bond followed by chemical reactions dominated by an organic peroxy radical (RO₂) and an alkoxy radical (RO). Ozone-driven oxidation of VOCs proceeds by the formation of ozonide and the decomposition of this compound, generating numerous products (Hao et al., 2011). Many thousands of oxygenated organic species possibly further undergo chemical reactions, resulting in changes in physicochemical and volatility properties (Paulsen et al., 2006; Baltensperger et al., 2005). For example, semi-volatile species oxidation may lead to low-volatility products in the atmosphere (Jimenez et al., 2009).

2.1.2 Anthropogenic sources

Anthropogenic aerosols are a mixture of primary particles and particles originating from gas-to-particle conversions. The combustion of coal, oil, gasoline, diesel and wood is an example of anthropogenic sources (Seinfeld and Pandis, 2006). Areas near highways suffer from high particle number concentrations which are result from traffic exhaust emissions, resuspension of dust and mechanical processes of brake wear and road-tyre interaction. Major pollutants in the vicinity of highways are fine particles, coarse-mode dust, gaseous NO_x and hydrocarbons. Other examples of major emission sources are industry (gaseous SO₂) and biomass burning (BC, gaseous CO, PAH). Examples of PAH sources are related to incomplete combustion in residential heating (wood, coal, oil, gas), gasoline engines, industrial boilers and forest fires (Peters et al., 1981; Ramdahl et al., 1983; Wang et al., 2016). Anthropogenic primary aerosol in the atmosphere consist mainly of soot agglomerates and fly ash, both from incomplete combustion processes.

Gaseous anthropogenic emissions and their oxidation reactions lead to secondary aerosol formation. For example, gaseous SO₂ emissions form SO₃, which then forms sulfuric acid via chemical reactions in the atmosphere. This acid can further form new particles by binary and ternary nucleation (Kulmala et al., 2000; Arnold et al., 2006 and 2012; Pirjola et al., 2015). Anthropogenic VOCs (AVOCs) comprise multiple different compounds; examples are aliphatic and aromatic hydrocarbons such as toluene and benzene, alcohols such as ethanol, n-butanol, and propanol, glycols, ethers, esters, ketones, aldehydes and organic acids such as formic acid. Some anthropogenic VOCs are closely related to health issues indoors; examples are benzene (from traffic); formaldehyde from glues and carpets and formic acid from air fresheners). In Finnish boreal forest areas, annual anthropogenic VOC emissions were two times smaller than forest emissions (Lindfors et al., 2000; Tarvainen et al., 2007).

Photolysis and initial reactions of VOCs with OH and NO₃ radicals lead to the formation of alkyl or substituted alkyl radicals. The reactions of ozone with alkenes and other

C=C bonds containing VOCs lead to the formation of organic peroxy radicals (RO₂) (Atkinson, 2000). Organic nitrates, RONO₂, can form via the reaction of organic peroxy radicals from biogenic or anthropogenic sources with gaseous NO:



The above equations are reaction channels that occur between organic peroxy radical and NO, NO₂ and HO₂ radicals. Equations 1, 2 and 4 leads to the net formation or destruction of ozone that depends on whether RO₂ react with NO or HO₂ (Atkinson, 2000). Equation 2 is a pathway that can form organic nitrates, being a sink for both RO₂ and NO. In Equation 3, thermal decomposition occurs at near room temperature for alkyl peroxy nitrates back to reactants being not important reaction channel in the lower troposphere (Atkinson, 2000). In addition, ONs can be formed from the oxidation of VOCs by NO₃ in nocturnal chemistry:



2.2 The composition of atmospheric aerosols

Atmospheric aerosol particles typically consist of carbonaceous matter, inorganic compounds, water and metals. Carbonaceous particulate matter consists of elemental carbon (EC), carbonate minerals, and a wide variety of organic compounds. In the atmosphere, with particulate matter <1 μm (PM₁), the main inorganic constituents are sulfate, nitrate, ammonium and chloride; slight amounts of sodium, potassium and calcium also exist (Seinfeld and Pandis, 2006). Refractory ash consists of metals and is released for example from combustion processes into the atmosphere. Particle chemical composition is influenced remarkably by physicochemical processes, condensation and evaporation. At various locations, in the non-refractory submicron aerosol mass in the atmosphere, organics cover 18-70%, sulfate 10-67%, nitrate 1.2-28%, ammonium 6.9-19% and chloride <4.8% (Kanakidou et al., 2005). Generally, the composition of the particles can vary a lot in different location and at different altitudes.

2.2.1 Inorganic compounds

In the atmosphere, submicron inorganic particulate matter can be, for example, in the form of ammonium sulfate ((NH₄)₂SO₄), ammonium bisulfate (NH₄HSO₄), potassium sulfate (K₂SO₄), ammonium nitrate (NH₄NO₃), potassium nitrate (KNO₃) sodium nitrate (NaNO₃), and ammonium chloride (NH₄Cl). In addition, inorganic compounds can be in acidic form as sulfuric acid (H₂SO₄). Typically, in the northern hemisphere, submicron aerosol particles mainly exist as a neutralized form of either ammonium sulfate (AS) or ammonium nitrate (AN) (Jimenez et al., 2009).

2.2.2 Organic compounds

At various locations in the northern hemisphere, organic compounds form the bulk of sub-micron aerosol mass (Jimenez et al., 2009). Organic compounds, hereafter organics, are compounds consisting of carbon-carbon bond. In addition to carbon atoms, organics contains other atoms bound to a carbon ion, i.e. hydrogen, oxygen, nitrogen, sulfur, and chloride, all of which can form functional groups of organics such as acids, alcohols, alkenes, ketones. Fresh organics, for example, from traffic are water-insoluble; aged organics, with their ability to absorb water from the gas phase, are more soluble (Jimenez et al., 2009). Organics detected by AMS consist of numerous fragmented organic ions; in the analysis, polycyclic aromatic hydrocarbons (PAHs) are separated into a group of their own.

Based on their sources in AMS data analysis, organics can be divided into smaller subgroups by PMF analysis (Paatero and Tapper, 1994; Paatero, 1997, Ulbrich, 2009). Groups can be separated by the O:C ratio, oxidation ratio, according to the amount of oxygen and carbon molecules in measured organic compounds (Aiken et al., 2007). The oxidation ratio is positively correlated with aerosol volatility (Jimenez et al., 2009; Ng et al., 2010). The H:C ratio is the ratio of hydrogen to carbon molecules in the organic compounds measured. The O:C ratio is a marker of the aging of organic aerosol in the atmosphere. In the following list, O:C ratios exhibit progressively greater oxygenation and consequent elevated processing time in the atmosphere: Hydrocarbon-like Organic Aerosol (HOA), other OA, Semi-Volatile Oxygenated Organic Aerosol (SV-OOA), Total Oxygenated Organic Aerosol (Total OOA) and Low-Volatile Oxygenated Organic Aerosol (LV-OOA) (Zhang et al., 2005a). Compared to their O:C ratios, the H:C ratios of these factors are inverse. The factors HOA, Biomass Burning Organic Aerosol (BBOA) and Cooking Organic Aerosol (COA) are primary aerosol components. HOA with a low O:C ratio (0.13 in a few studies) consists mainly of a hydrocarbon series ($C_nH_{2n+1}^+$) in the mass spectrum (MS) and originates directly from the emission source (i.e. traffic) with a diurnal trend (Crippa et al., 2014, Canagaratna et al., 2015). COA has an O:C ratio of 0.22 and is fresh organic aerosol; its diurnal trend follows anthropogenic activities. BBOA has an O:C ratio of 0.36 and, in the MS, has levoglucosan ($C_2H_4O_2^+$) as a marker/tracer of biomass burning (Aiken et al., 2010, Canagaratna et al., 2015). Secondary aerosol factors have higher O:C ratios: SV-OOA 0.53, total OOA 0.67, and LV-OOA 0.84 (Canagaratna et al., 2015). SV-OOA is semi-volatile aerosol, mainly originate from local sources, and exhibit a diurnally higher mass loading during night-time. In MS, SV-OOAs display remarkable peaks of $C_2H_3O^+$ (m/z 43) and $C_4H_7^+$ (m/z 55). LV-OOA is low-volatile aerosol with a high ion fragment of CO_2^+ (m/z 44) in MS and long-range transported aerosol. In addition, due to photolysis during day-time, LV-OOA mass loading increases diurnally.

Organic nitrates are semi-volatile, mainly formed via the reaction of peroxy radicals (RO_2) with NO through photochemistry (See Equation 2). They are also formed through the oxidation (NO_3 radical oxidant) of VOCs (See Fig. 2) (Atkinson, 2000). Submicron particulate organic nitrates form a small group among organic compounds in the atmosphere, below 2% of total submicron aerosol mass (papers II and III). In laboratory experiments, organic nitrate yields vary widely, depending on the VOC precursors (Ng et al., 2008; Fry et al., 2009 and 2011). Daily variations of ON are controlled by the ambient NO_x level (Browne, 2013), photochemistry and nocturnal dark chemistry (Fry et al., 2013; Day et al.,

2009), temperature (Day et al., 2008) and loss from deposition, hydrolysis and further oxidation (Liu et al., 2012).

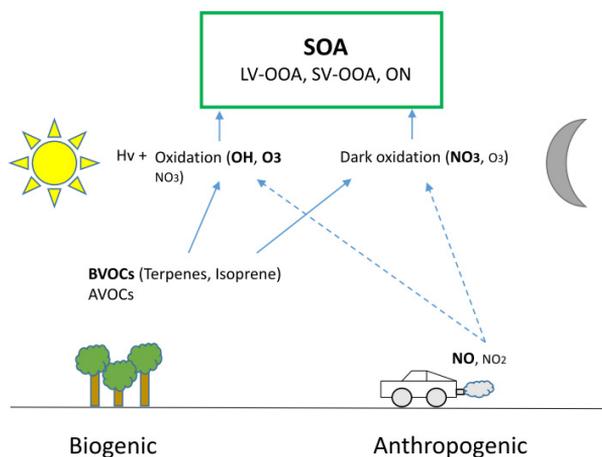


Figure 2: Secondary organic aerosol and organic nitrate formation.

2.2.3 Refractory compounds

Refractory compounds are low-volatile ones, that require high vaporization temperatures to be detected by AMS. SP (Soot Particle)-AMS is capable of measuring the chemical composition of the refractory components of laser-light absorbing particles in real time (Onasch et al., 2012). From refractory components, elemental carbon includes black carbon, carbon black and engineered carbon-based materials (Long et al., 2013). In the atmosphere EC is usually referred to as BC that is refractory particulate matter emitted directly from its sources, i.e. the incomplete combustion of both fossil fuels and biomass burning (Seinfeld and Pandis, 2006). Ash compounds originate from coal combustion; they are referred to fly ash as they are transported by flue gas. In wood combustion appliances, ultrafine (< 100 nm) ash particles are mainly composed of K, S and Zn; small amounts of C, Ca, Fe, Mg, Cl, P and Na also exist. Larger agglomerates mainly comprise carbon and are primarily soot particles (Tissari et al., 2008).

3 Materials and methods

3.1 High resolution time-of-flight aerosol mass spectrometer

The Aerodyne High-Resolution Time-Of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) is a tool for measuring size-resolved non-refractory aerosol particles chemical composition in real time (see Fig. 3). In AMS aerosol particles are introduced into vacuum chamber where the particles are accelerated by aerodynamic lense, chopped and flash-vaporized. The vaporization is performed by heater with standard temperatures of 600° C. (Jayne et al., 2000; Jimenez et al., 2003). The vaporized molecules are ionized and then formed ion fractions are quantified by time-of-flight mass spectrometer. In high resolution, the ion fragments can be elementally separated using the molecular ratios of C, O, H, N and S, enabling the calculation of, for instance, their O:C, H:C and N:C ratios (DeCarlo et al., 2006). Typically, this instrument detects the time series of particulate organics, sulfate, chloride, nitrate, ammonium and PAH compounds and their vacuum aerodynamic diameters from size range of 40-1000 nm (Jayne et al., 2000).

The latest feature SP-AMS has a laser vaporizer in addition to the heater used in previous versions (i.e. HR-ToF-AMS). SP-AMS uses the laser-induced incandescence of absorbing material, such as soot, to vaporize both the coatings and absorbing cores, measuring the mass of the refractory cores. In the case of soot, the refractory BC mass loading can be measured among the non-refractory species (Onasch et al., 2012).

3.1.1 Operation

AMS quantifies the chemical composition of particle ensembles using constructed mass spectra (MS). It also quantifies size of particle ensemble using particle time-of-flight (ToF). As particles are directed into AMS vacuum chamber, first the particles are focused into the diameter of 1 mm-sized beam by using an aerodynamic lens; by gas expansion in the lens, they develop size-dependent velocities (Zhang et al., 2002 and 2004). The narrow particle beam is modulated by a rotating chopper wheel that is operated at three separate positions: open, closed and chopped. Open position allows aerosol particles to enter heater freely. Closed position blocks the aerosol particle beam to encounter the heater and defines the background signal. By the difference of open and closed position, it is possible to define signal without effect of background. At chopped position, particle beam is directed through the chopper wheels two narrow slits enabling a 2% duty cycle at 100 Hz (Jimenez et al., 2003). Particle size is derived from ToF over the distance from choppers slits to heater. The heater is a tungsten cylinder with an embedded surface; at a standard temperature of 600° C, the particle beam is flash-vaporized (Jayne et al., 2000). Vaporized molecules are electron impact ionized using a beam of 70 eV electrons. The fragmentation of ions is well-known due to laboratory tests and theory and taken into account in analysis by fragmentation table described in Allan et al. (2004).

Positively charged ion fragments are separated by ToF mass spectrometer such as the Tofwerk AG orthogonal one into two operating V- and W-modes (see Fig. 3) (DeCarlo et al., 2006). The former has better sensitivity while the latter has better mass resolution. With

a mass range of 1-1200 m/z, the detection limit of the V-mode is 0.003 $\mu\text{g}/\text{m}^3$ and that of the W-mode is 0.05 $\mu\text{g}/\text{m}^3$; with the same range, the mass resolving power ($m/\Delta m$) of V is 2000 and that of W is 4000 (Aerodyne Research Inc., 2015).

Inside the mass spectrometer, ion fragments are operated by electric fields. Using a stable acceleration potential difference and assuming the flight distance as constant, the only changing value is mass to charge, which is used to separate ion fragments on detection. Flight pathways are divided into two: in the V-mode, ions undergo one curve from the reflector to the detector; in the W-mode, ions undergo two curves from the reflector and one curve from the hard mirror and to the detector over a longer flight distance (See Fig. 3). This longer flight distance spreads the ion beam and makes the mass-to-charge range more accurate. Finally, a multichannel plate aids in both detection and signal amplification.

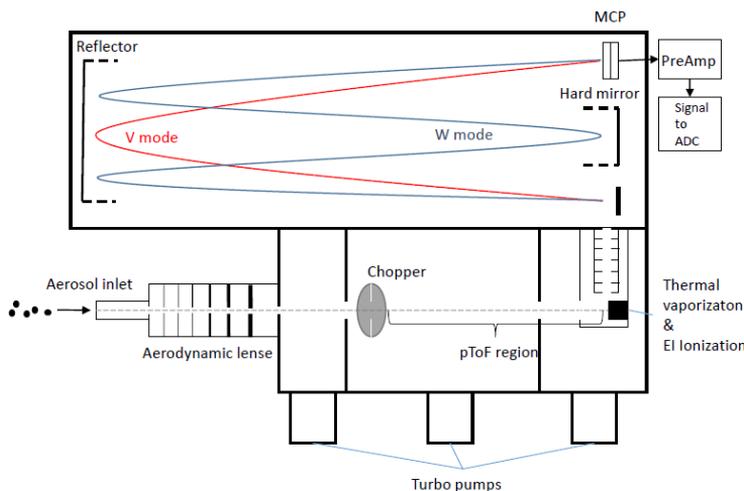


Figure 3: Schematics of HR-ToF-AMS operation.

Calculation of mass loadings of species C_s ($\mu\text{g}/\text{m}^3$) from ion signals I_s (ion counts/s) is defined by equation:

$$C_s = 10^{12} \frac{MW_s}{IE_s} \frac{I_s}{QN_A}, \quad (7)$$

where MW_s is molecular weight of species, Q (cm^3/s) is volumetric sample flow rate into the instrument, N_A is Avogadro's constant and IE_s is ionization efficiency of species (Jimenez et al., 2003). IE is a dimensionless quantity denoting the ratio of ions detected to the number of available desorbed molecules of the parent chemical species (Allan et al. 2003). The IE value is determined in the IE calibration procedure for ammonium nitrate (AN), the vaporization and fragmentation of which is well known in AMS. Mass concentration calculation depends also on Relative Ionization Efficiency (RIE) which is determined as

$$RIE_s = \frac{IE_s}{IE_{NO_3}} \frac{MW_{NO_3}}{MW_s}, \quad (8)$$

where IE_s is ionization efficiency and MW_s molecular weight of species in question and IE_{NO_3} is ionization efficiency and MW_{NO_3} molecular weight of nitrate (Jimenez et al., 2003). Default values for RIE are as follows: nitrate 1.1, sulfate 1.2, chloride 1.3, and organics 1.4. The RIE value for ammonium is derived from IE calibration. In practice, an increase in the RIE of ammonium artificially decreases the mass concentration of NH_4^+ and increases the acidity of the particles involved. Particle Collection Efficiency (CE) is applied to species mass loadings calculation to take into account the loss of particles from the aerodynamic transmission lens to detector (Alfarra et al., 2004). Mass loading of species C_s' ($\mu g/m^3$) is then

$$C_s' = C_s \frac{1}{CE_s}, \quad (9)$$

where CE_s is collection efficiency of species in question. Usually, CE is kept constant at 0.5; however, for example, if the ammonium nitrate mass fraction exceeds 0.4 in ambient measurements, CE can be applied as a composition-dependent algorithm as described in Middlebrook et al., (2012). In addition the size calibration of AMS involves determining vacuum aerodynamic diameters from velocity measurements of known monodisperse particulate aerosol (ammonium nitrate and polystyrene latex particles).

3.1.2 Data analysis

Data analysis was conducted using Igor Pro 6 software (Wavemetrics Inc., Lake Oswego, OR), PIKA (Peak Integration by Key Analysis), and SQUIRREL (SeQUential Igor data RetRIeval), user interfaces. HR analysis was conducted using PIKA and Unit Mass Resolution (UMR) using SQUIRREL. AMS chemical composition was calculated by using a constant CE of 0.5 for organics, chloride, sulfate, nitrate and ammonium. The relative ionization efficiencies were the default values: organics 1.4, chloride 1.3, sulfate 1.2, nitrate 1.1; the values for ammonium: 4 (paper I), 2.28 (paper II), 3.7 (papers III and IV), were determined from the calculation of ionization efficiency (IE) based on the calibration. In the laboratory experiments, concentration of gaseous CO_2 was monitored and applied to correct the gaseous fraction in the ion fragment CO_2^+ . In addition, in the laboratory experiments, mass loadings were corrected by a time-dependent dilution factor.

Organics were divided into smaller subgroups using the mathematical method of PMF (Paatero and Tapper, 1994; Paatero, 1997, Ulbrich, 2009). The PMF model defines the mass balance of constant source profiles (mass spectra for organics) and varying concentrations of profiles over the time measured (Ulbrich et al., 2009). The factors, which when combined replicate the overall organic mass spectrum and its time evolution, are determined by assessing residuals and model error, the Q-value, and comparison to external data sets (i.e., trace gases, particulate inorganics and other site mass spectra). Increasing the number of

factors results in the Q-value, which represents the error, decreasing slowly towards one. At this point, the error estimation of the residuals and the model error are equal.

Inorganic compounds were estimated using the principles of aerosol neutralization and molecular thermodynamics. Several neutral molecules such as $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , H_2SO_4 , NH_4NO_3 , NH_4Cl and other possible non-refractory molecular species that evaporate at a temperature of 600°C can be reconstructed from AMS measurements of inorganic species; the calculation requires several rules. The back-calculations of molecular compounds need to be estimated according to the ammonium to sulfate molar ratio in such a manner that all ammonium reacts first with sulfate (McMurry et al., 1983; Du et al., 2010). If $0 < \text{NH}_4/\text{SO}_4 < 1$, NH_4 exists in the chemical forms of H_2SO_4 and NH_4HSO_4 . If $1 < \text{NH}_4/\text{SO}_4 < 2$, NH_4 exists as $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . If the $\text{NH}_4/\text{SO}_4 > 2$, NH_4 participates with SO_4 first, and the rest reacts with NO_3 and Cl . The rest of NO_3 not neutralized by NH_4 is in the form NaNO_3 or organic nitrate. The calculation of organic and inorganic nitrates was based on equations (10)-(15).

$$NO_{Org}^+ = NO^+_{Org_factor1} + NO^+_{Org_factor2} \quad (10)$$

$$NO_{2,Org}^+ = NO_2^+_{Org_factor1} + NO_2^+_{Org_factor2} \quad (11)$$

$$NO_{Inorg}^+ = NO^+_{Org_factor3} \quad (12)$$

$$NO_{2,Inorg}^+ = NO_2^+_{Org_factor3} \quad (13)$$

$$NO_{3,org} = (NO_{Org}^+ + NO_{2,Org}^+)/0.96 \quad (14)$$

$$NO_{3,inorg} = (NO_{Inorg}^+ + NO_{2,Inorg}^+)/0.96 \quad (15)$$

where $NO_{3,org}$ refers to organic nitrate masses and $NO_{3,inorg}$ to inorganic ones. NO_{Org}^+ and $NO_{2,Org}^+$ are the mass concentrations of NO^+ and NO_2^+ ions in Org factors 1 and 2, and NO_{Inorg}^+ and $NO_{2,Inorg}^+$ are the mass concentrations of the same ions in Org factor 3. The four latter variables can be directly obtained from PMF results.

3.2 Measurements

The present study involved field measurements at two separate sites which focused on tracking ambient aerosol particles. The laboratory measurements focused on direct particulate emissions of wood combustion. In all measurements in front of the AMS inlet, to eliminate the possible effect of water content on aerosol mass quantification, aerosol samples were dried using a Permapure Nafion® dryer or a silica-gel dryer. An extra suction of 1 l/min was created in the AMS sampling line by adding another device (particle number concentration (CPC) or Differential Mobility Particle Sizer (DMPS)) or an external suction to reduce condensation on the sampling line. The AMS averaging time was set to 5 minutes in ambient measurements; in the laboratory, both 5 minutes and 1 minute were used as averaging times.

At ambient measurement sites, aerosol number concentration and size distributions in a size range of approx. 10-800 nm were measured using a DMPS. In addition trace gas constituents (O_3 , NO_x , SO_2 , CO , CO_2), meteorological parameters (wind speed, wind direction, precipitation, temperature, and relative humidity) and black carbon mass concentration were measured. Air trajectories were computed using the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model (Draxler et al., 2013; Rolph et al., 2013).

In laboratory experiments, measuring emissions of wood combustion, flue gas was diluted prior to aerosol sampling with a porous tube diluter and two ejector diluters in a series. Dilution ratios in the experiments varied from 500 to 2000, depending on sampling location and combustion conditions. Gas phase species (O_2 , CO , CO_2 , NO_x , C_xH_y) were monitored directly from the stack by a Fourier Transform Infrared Spectroscopy (FTIR) method. Total number concentration was measured with a CPC.

3.2.1 Field measurements on SMEAR II site

Measurements were conducted at Hyytiälä ($61^\circ 51'N$, $24^\circ 17'E$) in southern Finland on SMEAR II site (Station for Measuring Forest Ecosystem-Aerosol Relations) during early spring 15.3-20.4.2011 (Hari and Kulmala, 2005) (paper II). The site is located on a hill (180m ASL) surrounded by boreal forest (mainly pine, spruce, birch and aspen). Agriculture exists in the vicinity of the site and the Juupajoki village 6 km south-east. The densely populated Tampere city area lies approximately 50 km south-west.

PMF analysis was conducted for organic and error matrices of HR in an m/z range of 12-150 amu. For PMF analysis, the time series and errors of NO^+ and NO_2^+ ions were integrated into the organic and error matrices. The PMF was evaluated using factors ranging from one to ten; the rotational parameter F_{peak} value was varied from -1.0 to 1.0, 0.2 at a time. Previously reported MS profiles and supporting measurement data from other instruments and campaigns aided in the interpretation of PMF results. As additional factors provided no extra information and the residuals were low (Q-value 3.97), our final solution was a 3-factor solution. Based on a comparison with external tracers, the F_{peak} was fixed at 1.

3.2.2 Field measurements on SMEAR IV site

The measurements were performed at SMEAR IV station located at a top of Puijo tower (306 ASL) in Kuopio ($62^\circ 54' 34'' N$, $27^\circ 39' 19'' E$) in central Finland during the autumn 21.9-27.10.2010 (Leskinen et al., 2009) (papers III and IV). The station is 224 m above the level of the lake nearby, and it is surrounded by boreal forests (mainly pine, spruce and birch). The city center of Kuopio lies approximately 2 km south-east. The most important local anthropogenic sources are traffic, a district heating plant, a paper mill, and residential areas in and around the city (Portin et al., 2014). The measurement station is located in a unique semi-urban region, sharing an opportunity to observe anthropogenic and biogenic aerosols and their interactions. For a more detailed description of the station and instrumentation, see Leskinen et al. (2009, 2012) and Portin et al. (2009, 2014).

Regarding to cloud events, which were, as measured using a cloud droplet probe (CDP), characterized by a sudden drop in visibility and a burst of cloud droplets (paper IV). Two parallel lines were used for aerosol samplings. The first one was a total inlet line with

a maximum cut-off size of 40 μm . The inlet was heated to 40° C to dry the cloud droplets, consequently, it was possible to obtain the total cloud particles (TOT), including both cloud interstitial particles (INT) and cloud droplet residuals (RES). The other was a PM₁ sampling line; within this line, in order to remove cloud droplets, an impactor with a 1 μm cut-off size was installed. This latter line provided information on INT particles. The cloud residual particles were estimated according to the DMPS data removing PM₁ sampling lines data from the dried cloud droplet data (See Fig. 4). During cloud events, the AMS sampling line was manually switched between the two alternative sampling lines. Most of the time, AMS measured from the TOT sampling line. In addition the whole campaign excluding the cloud events was characterized in detail (paper III).

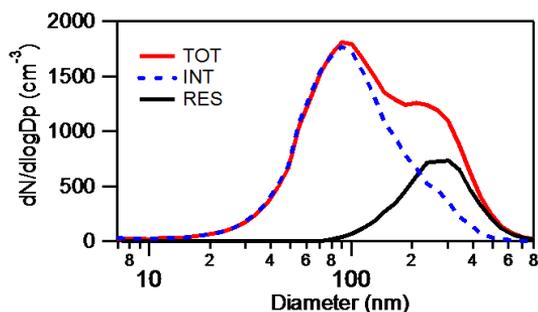


Figure 4: Cloud droplet residuals (RES) estimation from the average number size distributions by DMPS during the cloud event (captured from paper IV).

In PMF analysis, organic and error matrices were analyzed in the mass range of 12–150 amu; in addition, NO⁺ and NO₂⁺ ions and their errors were integrated into the matrices. PMF was evaluated using factors ranging from one to ten, and F_{peak} was varied from –1 to 1 in steps of 0.1. After the evaluation of MS, time series and correlations with other tracers, a five-factor solution explained the PMF outcome best. Because no good correlation was detected with gas or particulate measurements, two factors in the five-factor solution were merged using a mass-weighted combination to generate a new factor. This new combined factor had a good correlation with the time series of nitrate species. Adding more factors in the PMF resulted in the solution producing meaningless factors. We finally chose a four-factor solution. The factor time series displayed the best correlations with tracers at F_{peak} 0.1.

3.2.3 Laboratory experiments

Wood combustion experiments were conducted in a laboratory at the University of Eastern Finland, Kuopio, during October and November, 2010. Wood chips, which had roughly 10% moisture content and were a mixture of spruce and deciduous wood, were burned in a moving step-grate burner (Ariterm Multijet, 40 kW) under different combustion conditions, and the emission products were measured directly. These wood chips were added into the heater periodically; every 20 minutes, the grate elements moved automatically, facilitating

ash removal from the grate. Combustion conditions were controlled by adjusting fuel feeding and air staging. Based on the emission rates of carbon monoxide (CO), the experiments were divided into those possessing efficient (low CO), intermediate (elevated CO), and smoldering (high CO) combustion conditions. Based on the CO concentration level, the process of biomass burning in a modern pellet boiler exemplifies efficient combustion; conventional batch combustion conditions typify smoldering; and intermediate combustion conditions include both these conditions; a malfunction of a continuously working burner is a good example.

Data processing for AMS species was obtained at HR in an m/z range of 12-198 amu to determine the mass concentrations of organics, sulfate, chloride, nitrate and ammonium. PAH species were analyzed in the range of 198-453 amu in UMR. Particle size distributions were defined for organics and PAH. Organic and error matrices in an m/z range of 12-198 amu underwent PMF analysis. The chosen 8-factor solution had a Q-value of 2.90. A rotational parameter F_{peak} value of 0.6 was chosen as it best distinguished between MS profiles. Two factors in the 8-factor solution were highly similar in MS patterns and time series. Hence the two were merged using a mass-weighted combination. Two other factors were factor combinations themselves. As they included less than 20% of the organics signal and they revealed no new information in the analysis, they were excluded from further analysis. The final PMF outcome consisted of five distinct factors.

4 Results

4.1 Chemical composition of submicron aerosol particles in the boreal forest area

The average mass concentration was $1.80 \mu\text{g}/\text{m}^3$ at the boreal forest SMEAR II site and slightly higher ($2.47 \mu\text{g}/\text{m}^3$) at the boreal forestland-urban mixed SMEAR IV site. Of the PM_1 mass fraction at both sites, organics and sulfate accounted for roughly two thirds; the remainder comprised ammonium, nitrate, black carbon and chloride (See Table 1). These proportions were at a level similar to that of the boreal forest area in Allan et al., (2006) and Raatikainen et al., (2010). During the cloud event at SMEAR IV, from the TOT sampling line, organics and sulfate accounted for almost 85% of submicron aerosol mass. The higher average mass concentration ($5.80 \mu\text{g}/\text{m}^3$) during the cloud events was evitable due to the increased particle mean size (paper IV).

During cloud events, all cloud interstitial particles, mixed cloud interstitial and residual particles, which contained inorganics were divided into ammonium nitrate (NH_4NO_3) and neutralized and acidic sulfate; this division was based on the neutralization criteria and calculations described in section 3.1.2 and in more detail in paper IV. Sulfate occurred mainly in acidic form (NH_4HSO_4) in cloud interstitial particles while neutralized sulfate ($(\text{NH}_4)_2\text{SO}_4$) dominated in cloud residual particles. During cloud events, the acidic form in INT particles was due to the fact that the partial pressure of ammonia on the surface of liquid particles is higher than the ambient pressure, causing ammonia to partly evaporate. Nitrate was mainly NH_4NO_3 in RES particles.

In the remote boreal forest area, sulfate occurred mainly in the form of ammonium sulfate and nitrate as ammonium nitrate (paper II). Ammonium sulfate served as a marker of long-range transported aerosol.

Table 1: Total mass loadings and average mass fractions of species at SMEAR II, IV and IV during the cloud event (TOT particles).

Site	Total mass ($\mu\text{g}/\text{m}^3$)	Org (%)	SO_4 (%)	NH_4 (%)	NO_3 (%)	BC (%)	Chl (%)
SMEAR II	1.8	49.0	22.0	10.0	7.0	11.0	<1
SMEAR IV	2.5	48.2	28.7	9.3	4.9	8.1	0.8
Cloud event	5.8	56.8	27.2	10.1	5.3	-	0.6

4.1.1 Biogenic and anthropogenic organic aerosol sources

At boreal forest and boreal forest-urban mixed region, PMF analyses for combined organics and NO^+ and NO_2^+ ions identified three factors: LV-OOA (Low Volatile-Oxygenated Or-

ganic Aerosol), SV-OOA (Semi-volatile OOA) and the NO-factor/NIA-factor (nitrate inorganic aerosol). At boreal forest-urban mixed region, SMEAR IV, in the vicinity of a populated area, PMF analysis also yielded HOA (Hydrocarbon-like Organic Aerosol), representing fresh organic aerosol. Organics were dominated by LV- and SV-OOA factors. Table 2 presents the mass fractions of the factors; ‘NO-factor’ represents both the NIA-factor and the NO-factor.

Table 2: Mass fractions of aerosol mass at SMEAR II and IV.

site	Organics			Inorganics
	LV-OOA (%)	SV-OOA (%)	HOA (%)	NO-factor (%)
SMEAR II	54.0	36.0	-	10.0
SMEAR IV	51.0	33.8	8.3	6.9

At boreal forest area, the MS patterns of LV-OOA and SV-OOA were similar to OOA1 and OOA2 components determined by PMF at the same measurement site by Raatikainen et al., (2010). The MS patterns were studied in more detail at the boreal forest-urban mixed region. LV-OOA represented highly oxygenated and long-range transported organic aerosol and its MS was dominated by the ion series of $C_xH_yO^+$ and $C_xH_yO_2^+$ with the highest peaks of CO^+ and CO_2^+ . The LV-OOA time series correlated well with ammonium sulfate ($R^2=0.6$) (paper II) and with sulfate ($R^2=0.56$) (paper III) (Fig. 5). The O:C ratios were 0.90 at boreal forest area and 0.74 at boreal forest-urban mixed region. The differences in the O:C ratios can be explained by the fact that, in paper II at boreal forest area, the O:C ratio was calculated considering the CHO^+ ion correction, which elevates the ratio (Canagaratna et al., 2015). When the older results from paper III are multiplied by the correction factor of 1.26 from Canagaratna et al., (2015), the O:C ratio of LV-OOA measured in boreal forest-urban mixed region at Puijo is 0.93, which is very close to values measured in boreal forest area at Hyytiälä.

At both measurement sites, based on the wind rose and back trajectory analysis, the major sources were long-range transported aerosol from southern wind directions (for example, southern Finland, southern Sweden and central Europe). Diurnally, LV-OOA started to increase gradually in the morning to peak in the afternoon, possibly related to increased photochemistry. Less oxygenated species were oxidized into more oxygenated forms. During cloud events, LV-OOA was present mainly in cloud residual particles (paper IV).

SV-OOA was dominated by the peak of $C_2H_3O^+$ and in general, the ion series of C_xH_y , $C_xH_yO^+$ and $C_xH_yO_2^+$ accounted for the majority of signals in MS. SV-OOA was less oxygenated (0.54 boreal forest area and O:C=0.41 boreal forest-urban mixed region), possibly fresh oxidized, organic aerosol. When the older results from paper III are multiplied by the correction factor of 1.26 from Canagaratna et al., (2015), the O:C ratio of SV-OOA measured in boreal forest-urban mixed region at Puijo is 0.52, hence very close to value measured in boreal forest area. In addition SV-OOA had a correlation with nitrate ($R^2=0.55$) (see Fig. 5).

Relative mass contributions of SV-OOA were higher in the north (paper III), aerosol particles from the north having spent less time above the continent and usually being freshly formed at boreal forest areas. The diurnal pattern of SV-OOA was related to boundary layer

dynamics, temperature and formation mechanism, peaking in the morning. SV-OOA dominated organics during the night-time, possibly associated with a decrease in temperature and SOA formation from nocturnal chemistry. The SV-OOA decrease in the afternoon may be due to both the increase of boundary layer height and possible evaporation of semi-volatile matter from particles; the evaporation, in turn, may be because of higher ambient temperature and lower relative humidity.

The diurnal behavior of SV-OOA was similar in both boreal forest area and boreal forest-urban mixed region. The anthropogenic influence on SV-OOA was observed in boreal forest area at SMEAR II as several high mass concentration peaks included in the time series; according to wind rose, this aerosol originated from the south-east, where the local sawmill factory (Juupajoki) is a major industry (Liao et al., 2011; Corrigan et al., 2013). The secondary conversion of sawmill factory emissions was presumably an important anthropogenic source that contributed greatly to the SV-OOA and organic nitrates observed.

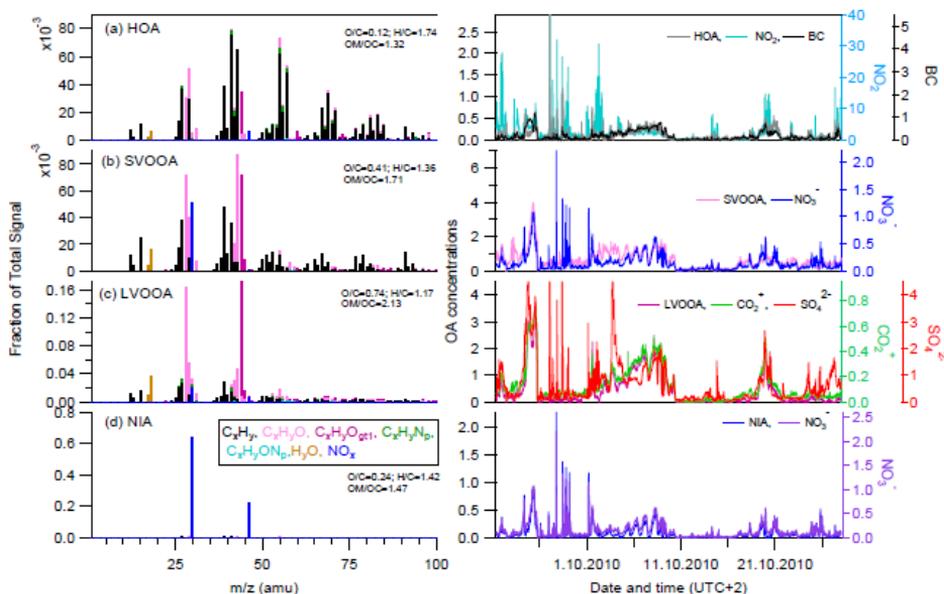


Figure 5: HR mass spectra profiles (left panel), time series and the correlations with the tracers (right panel) in SMEAR IV. The right axis has units of $\mu\text{g}/\text{m}^3$ (paper III).

In the boreal forest-urban mixed region, HOA was the local source ($\text{O}:\text{C}=0.12$) associating with combustion-related primary organic aerosol. HOA correlated with the ion fragment C_4H_9^+ ($R^2=0.93$), a tracer of primary combustion (Zhang et al., 2005a and 2005b), BC ($R^2=0.44$) and NO_x ($R^2=0.31$). The MS of HOA was dominated by the ion series $\text{C}_n\text{H}_{2n+1}^+$ and $\text{C}_n\text{H}_{2n-1}^+$ (see Fig. 5). HOA species originated from the wind directions of the city center, paper mill, highway and heating plant. The diurnal cycle of HOA was the result of the interplay between traffic and other multiple primary anthropogenic organic aerosol sources

such as cooking, biomass burning and direct industrial emissions. In addition, during cloud events (paper IV), HOA was found mainly in cloud cloud interstitial particles.

At boreal forest and boreal forest-urban mixed region were found inorganic factors representing ammonium nitrate. NO-factor was in line ($R^2=0.94$) with the time series of the NH_4NO_3 estimated (paper II). Thus, this factor was recognized as a NH_4NO_3 inorganic factor. The $\text{NO}^+/\text{NO}_2^+$ ratio of this factor depends on instrument settings; we obtained a 2.4 ratio. The $\text{NO}^+/\text{NO}_2^+$ ratio of the NIA factors was 2.9 (paper III), and these two ions formed 86.4% of the whole signal. Both ratios are consistent with recent results stating that the ammonium nitrates $\text{NO}^+/\text{NO}_2^+$ ratio ranges between 2 to 3 (Alfarra et al., 2006; Fry et al., 2009; Liu et al., 2012). Diurnally, ammonium nitrate (estimated NH_4NO_3 , NO- and NIA-factor) increased during the night-time, following boundary layer depth change and RH increase. With the increase in temperature and radiation during the day-time, semi-volatile ammonium nitrate evaporated from its particulate form.

4.1.2 Organic nitrates

The fact that NO_x^+ ion fragments divide into organic and inorganic factors indicates that nitrate (in the functional group form) has organic and inorganic chemical forms. When the $\text{NO}^+/\text{NO}_2^+$ ratio of a factor fell to 2-3, that factor represented mainly the inorganic form (described earlier in the text). The rest of the NO_x^+ ion fragments were divided among organic factors. For organic nitrates, the $\text{NO}^+/\text{NO}_2^+$ ratio was 8.5 at remote boreal forest area (paper II) and 10.4 boreal forest-urban mixed region (paper III); both were at the lower limit of values 10-15 found in laboratory chamber studies with reactions of monoterpenes and the nitrate radical in Fry et al., (2009) and Bruns et al., (2010). In boreal forest-urban mixed region more than 63% of the NO_x^+ ion fragment mass was apportioned to the inorganic NIA factor, while nearly 28% was in the SV-OOA factor and 9% in the LV-OOA. In boreal forest area, the percentages were 65% for the NO-factor, 30% for SV-OOA and 5% for LV-OOA. The calculation of the organic nitrate mass loading followed equations (10)-(15) in section 3.1.2.

Table 3: Organic nitrates' (ON) mass loadings, ON mass fractions of total organics and PM_{10} at the remote boreal forest area (the brackets in row I represent these values modified by the influence of anthropogenic sawmill plumes), the boreal forestland-urban mixed area (here, semi-urban), and the urban site (from literature).

	ON mass ($\mu\text{g}/\text{m}^3$)	ON fraction of total Org (%)	ON fraction of PM_{10} (%)
remote boreal forest	0.027 (0.033)	3.3 (3.6)	1.6 (1.8)
semi-urban	0.040	3.4	1.7
urban	0.8-1.6 ¹	9.5-19.0 ¹	4.0-8.1 ²

¹ Estimated ON mass loading in SOAR-1 campaign (Farmer et al., 2010).

² Calculated according to estimated ON mass in Farmer et al., 2010 and reported average mass loadings in Docherty et al., 2011 in SOAR-1 campaign.

In the remote boreal forest area at Hyytiälä, the average background mass concentration of organic nitrates was $0.027 \pm 0.028 \mu\text{g}/\text{m}^3$ (\pm s.d.), 1.6% of the PM_{10} (Table 3.). When the anthropogenic influence of occasional sawmill plumes was considered, the ON mass concentration was slightly higher ($0.033 \pm 0.057 \mu\text{g}/\text{m}^3$). In the boreal forestland-urban mixed area, 1.7% of PM_{10} was organic nitrates. The ON fraction of total organics was 3.3-3.6% in the boreal forest and urban mixed areas (Table 3). In the SOAR-1 (Study of Organic Aerosol at Riverside) campaign at an urban site in eastern Los Angeles, California, USA, Farmer et al., (2010) estimated ON mass loadings of 0.8-1.6 $\mu\text{g}/\text{m}^3$ and 9.5-19% ON fraction of total organics. Farmer et al. (2010) quantified ON through five pathways: (i) the NO_x^+ fragmentation ratio, (ii) fragmentation to HNO_3^+ ions, (iii) fragmentation to NO_x -containing organic ions ($\text{C}_x\text{H}_y\text{O}_z\text{N}^+$), (iv) the NH_4^+ balance and (v) the difference between total and inorganic NO_3 . Their results indicated an ON mass fraction of 4.0-8.1% of PM_{10} in the urban environment. Hence, the organic nitrate mass fraction of total organics and PM_{10} can vary highly between different locations.

In boreal forest-urban mixed region, 74.4% of organic nitrate was associated with SV-OOA, suggesting its semi-volatile property in nature. Of the rest, 24.3% associated with LV-OOA and 1.3% with HOA. In boreal forest area, at Hyytiälä, the percentages were similar (SV-OOA accounting for 77.7% and LV-OOA for 23.3%). ON exhibited a pronounced diurnal cycle characterized by a maximum at night and a minimum in the afternoon (Fig. 6). The average mass concentration during night-time was roughly double that during day-time, suggesting nocturnal formation as a major source of ON in remote boreal forest area. In boreal forest-urban mixed region, the mass concentration of ON was diurnally slightly higher than in remote boreal forest area. Higher mass concentrations were likely due to anthropogenic emissions from the city area at the vicinity. In addition, sawmill emissions at remote boreal forest area double momentarily ON mass loading during the night-time. In general, 88% of the particulate nitrate species from sawmill were composed of organic nitrate, highlighting the importance of anthropogenic activity in atmospheric organic nitrate formation. With the analysis on the wind rose, it was concluded that the major formation pathways of ON in Hyytiälä were from the chemical reaction between the biogenic VOC emissions, monoterpene compounds emitted from the sawmill (Liao et al., 2011), or both, and the anthropogenic NO_3 radical (as the result of the reaction of NO_2 and O_3). At Puijo station, surrounded by boreal forest, organic nitrates were likely associated with biogenic VOC emissions nocturnally oxidized by the nitrate radical.

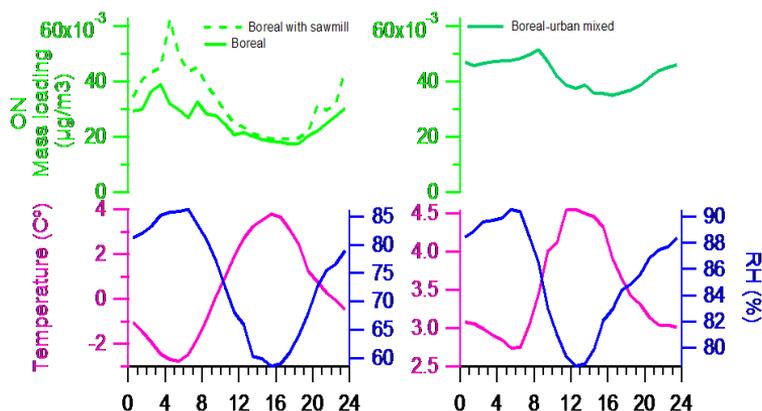


Figure 6: Diurnal cycles of particulate organic nitrates (ON) with (dashed line) and without (solid line) the air mass plumes from sawmill factory at boreal forest area and ON boreal forest-urban mixed region. Diurnal cycles of relative humidity (RH) and ambient temperature.

The participation of organic nitrates in the formation of clouds was studied during the cloud events at boreal forest-urban mixed region, where organic nitrates accounted for 26% of the total nitrate from cloud residual particles and 51% of the total nitrate from cloud interstitial particles (paper IV). In addition, the difference of the $\text{NO}^+/\text{NO}_2^+$ ratios between TOT (3.80) and INT (4.68) particles indicated the variability of organic nitrate content in cloud INT particles. Nitrates were distributed in PMF analysis only as ammonium nitrate and organic nitrates, indicating that the interference of nitrate signals from marine aerosols was most likely negligible; the $\text{NO}^+/\text{NO}_2^+$ ratio of NaNO_3 compounds is 29 in Rollins et al., (2010).

4.2 Direct combustion emissions

Organic aerosol sources were studied from direct particulate emissions from the combustion of wood chips in a moving step-grate burner in different combustion conditions (efficient, intermediate, smoldering). Organics were split into five distinct factors: Hydrocarbon-like Organic Aerosol (HOA), Low Volatile-Oxidized Organic Aerosol (LV-OOA), Biomass Burning Organic Aerosol (BBOA) and two novel factors, PAH (Polycyclic Aromatic Hydrocarbon) and Aromatics. In addition, a small amount of non-refractory inorganic species was detected in incomplete combustion conditions.

4.2.1 Combustion phases

In our study, in efficient combustion, the main constituents were ultrafine inorganic salt particles whilst, in intermediate and smoldering combustion, the main constituents were OC and EC. Because of a large fraction of soot compared to efficient combustion, intermediate and smoldering combustion produced particles mainly in the accumulation mode (Leskinen

et al., 2014). Furthermore, based on a morphological analysis of size-classified particles (Torvela et al., 2014), OC condensed on the surface of the ash and soot particles formed during intermediate and smoldering combustion conditions. In incomplete combustion conditions, both OC and particulate PAH emissions increased. Two burning phases occurred frequently in intermediate and smoldering combustion. Phase 1 occurred when, after new fuel addition, gaseous carbon oxide (CO) rapidly increased. With low CO emissions until the new fuel addition and automatic removal of fuel leftovers from the grate, phase 2 was a stable, burn-out period.

4.2.2 Aerosol sources

PAHs formed only during smoldering combustion. PAHs and LV-OOA formed mainly during the occasionally peaking CO emissions (Fig. 7). HOA, sulfate, nitrate and chloride exhibited similar peaking behavior; they also exist during stable combustion conditions. Nitrate originated mainly from inorganic salts and possibly from organic compounds including NO^+ ion fragments. Sulfate originated from oxidation reactions or the decomposition of inorganic salts such as K_2SO_4 . Chloride could have been a decomposition product from the inorganic salts emitted. BBOA was consistent with levoglucosan formation during combustion and became higher during stable combustion conditions. The aromatics factor formed mainly during stable combustion conditions while it occurred all the time in combustion emissions.

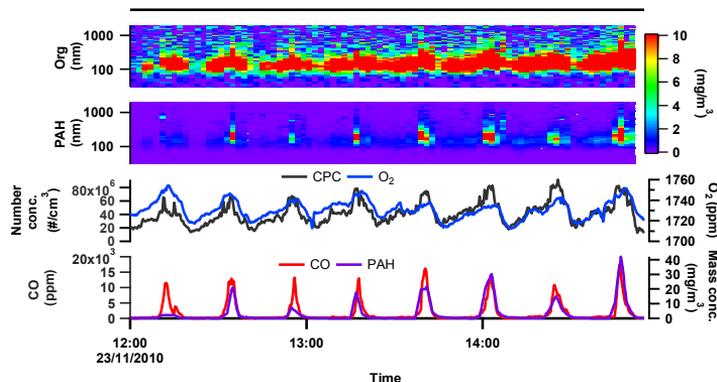


Figure 7: Size-resolved mass concentrations of organics (Org) and PAHs, particle number concentration (CPC) and concentrations of gaseous O_2 and CO in smoldering combustion. (modified from paper IV).

Perhaps due to the thermal decomposition of acids and highly oxygenated compounds in the AMS heater or carboxylic acids abundant in wood smoke, LV-OOA (O:C ratio of 0.63) represented highly oxidized organic aerosol. The highest peaks of the HOA (O:C ratio of 0.04) mass spectrums were C_3H_5^+ (m/z 41), $\text{C}_2\text{H}_3\text{O}^+$ (43), C_4H_7^+ (55), C_4H_9^+ (57) and other hydrocarbons in the $\text{C}_n\text{H}_{2n+1}$ series. The BBOA (O:C ratio of 0.17) factor was slightly

oxidized organic aerosol with the highest ion fragments of CHO^+ among other oxygen-containing ion fragments. The aromatics (O:C ratio of 0.04) factor was mainly composed of ion fragments containing aromatic rings; these fragments could have possibly formed from the n-butyl benzenesulfonamide compound ($\text{C}_6\text{H}_7\text{NO}_2\text{S}$) likely originating from phenols and methylated aromatics and condensing to particle phase. In the HR organic MS, PAHs were single charged at a mass range of 198-300 m/z and double charged at 100-198 m/z.

5 Review of papers and the author's contribution

Paper I evaluated the ability of HR-ToF-AMS to measure the chemical composition of non-refractory particulate matter from direct wood combustion emissions in real time from a moving step-grate burner. The combustion conditions were changed by adjusting fuel feeding and air staging in the burner to mimic biomass burning in a modern pellet boiler (the efficient combustion experiment), conventional batch combustion conditions (the smoldering combustion experiment) and in the intermediate combustion experiment with partly both conditions or a malfunction of the continuously working burner. In the intermediate and smoldering experiments, the addition of new fuel on the grate and the stable burning phase resulted in two separate combustion phases of momentarily peaking CO from less complete oxidation. The study revealed that organics were split into five distinct factors: HOA, LV-OOA, BBOA, all three with characteristics from ambient measurements, and two new factors, PAH and Aromatics. PAH compounds formed only during momentarily peaking CO in smoldering combustion. The aromatics factor was mainly composed of ion fragments containing aromatic rings likely originating from phenols and methylated aromatic compounds, both of which form during stable burning.

I was the main author of the paper. I participated in planning of campaigns, performed AMS measurements, calibrations, maintaining processes and conducting data analysis discussions with colleagues and analyzed the AMS data. In addition, I contributed to the general data analysis and scientific discussions with colleagues.

Paper II focused on tracking particulate organic nitrate sources in a boreal forest area in southern Finland in spring, 2011. Measurements were conducted using HR-ToF-AMS. Using PMF, we analyzed integrated organics and nitrate ions and identified the organic factors of SV-OOA and LV-OOA and the inorganic NO factor. The NO factor mainly represented ammonium nitrate, and the excluded parts of nitrate ions were divided into organic factors. Organic nitrates were mainly semi-volatile in nature, formed by nocturnal chemistry by the reactions of the NO₃ radical and biogenic VOCs from forests. Organic nitrate mass loading was roughly double during the night-time. In addition, the local sawmill factory occasionally influenced organic nitrate formation, with 88% of nitrate emissions being organic.

I had a main responsibility of writing the paper. I also participated in planning of campaigns, AMS measurements, calibrations, maintaining processes and analyzed the AMS data. I also had a main responsibility on data interpretation and the scientific conclusions.

Paper III focused on source apportionment of anthropogenic and biogenic aerosol particles and their possible interactions in a semi-urban location. HR-ToF-AMS measurements were

conducted in the vicinity of Kuopio town surrounded by boreal forest in central Finland in autumn, 2010. The same data set was used in **papers III** and **IV**. In **paper III**, organics and nitrate ions were integrated for PMF analysis and MS patterns were described in detail. LV-OOA represented highly oxygenated and long-range transported organic aerosol; SV-OOA was less-oxygenated possibly fresh oxidized organic aerosol; HOA (Hydrocarbon-like Organic Aerosol) was the local source in the semi-urban atmosphere associated with combustion-related primary organic aerosol. The inorganic factor NIA (Nitrate Inorganic Aerosol) represented ammonium nitrate. More than 63% of nitrate ions mass was apportioned to the NIA factor and the rest mainly to SV-OOA. Of organic nitrate, 74.4% was assigned to the SV-OOA component, suggesting its semi-volatile property in nature. Organic nitrates were likely formed by the nocturnal chemical reactions of the NO_3 radical and biogenic VOCs (Volatile Organic Carbon) from the surrounding forest. The diurnal pattern of LV-OOA exhibited a gradual increase in the morning to peak in the afternoon, possibly related to increased photochemistry. Diurnally, SV-OOA was related to boundary layer dynamics, temperature and formation mechanisms. SV-OOA dominated organics during the nighttime. The diurnal cycle of HOA was related to primary anthropogenic sources from the town (traffic, cooking, industrial emissions, and biomass burning). NIA was diurnally similar to SV-OOA.

Paper IV focused on characterizing the chemical composition of aerosol during cloud events. During cloud events, aerosol samples were split into cloud INT particles and cloud RES particles by data analysis from an automated valve system shifting between a total sampling line with a cut-off size of $40\ \mu\text{m}$ and a PM_{10} line within which an impactor was installed with a cut-off size of $1\ \mu\text{m}$. Acidic sulfate (NH_4HSO_4) occurred mainly in INT particles while neutralized sulfate ($(\text{NH}_4)_2\text{SO}_4$) dominated in RES particles. HOA and SV-OOA were higher in INT particles while LV-OOA was higher in RES particles. In PMF calculations, organic nitrates accounted for 26% of the total nitrate from RES particles and 51% of the total nitrate from INT particles, the rest being ammonium nitrate. Differences in chemical composition relate to particle size effects, cloud droplet activation and partitioning mechanisms between the gas and particle phases within and without the cloud.

In papers III and IV, I participated in planning of campaigns, AMS measurements, calibrations and maintaining processes. I also participated in PMF analysis and contributed to data interpretation and scientific discussions.

6 Conclusions

We conducted HR-ToF-AMS measurements in laboratory experiments on wood combustion and at two ambient locations, a remote boreal forest area and a boreal forestland-urban mixed region. The PMF analysis method (Paatero and Tapper, 1994; Paatero, 1997, Ulbrich, 2009) was used for the first time to split both organics from direct combustion emissions source (paper I) and, to the best of our knowledge for the first time, integrated organics and nitrate ions (papers II, III, IV), into factors representing aerosol sources with biogenic and anthropogenic characteristics.

The first objective was to examine sources of organic aerosol particles in a boreal forest environment and a boreal forestland-urban mixed region. O:C ratios and mass spectral patterns of oxygenated factors were very similar in both boreal forest areas, hence the factors were comparable and they represented a similar organic sources. SV-OOA, LV-OOA and HOA adequately represent the organic aerosol sources from the boreal forest area. SV-OOA is mainly biogenic-based; LV-OOA, with its high aging time in the atmosphere, influences both biogenic and anthropogenic sources; and HOAs are solely related to anthropogenic emissions. The factors characterized in high resolution were in good agreement with previous studies at the same boreal forest site (Raatikainen et al., 2010 and Finessi et al. 2012) and other locations (Zhang et al. 2005a; 2005b and Nq et al., 2010).

The second objective was to investigate, by measuring organic nitrates, anthropogenic-biogenic interactions. Anthropogenic emissions (traffic, industry) affected organic nitrate formation by forming the NO_3 radical oxidant. Particulate organic nitrates were thus a result of the chemistry between gaseous anthropogenic emissions and biogenic VOC emissions from the forest. Organic nitrates were mainly semi-volatile in nature, and they decreased during the day-time due to the impact of the rapid decomposition of the nitrate radical under UV irradiation. Our new analysis method detected slight amounts of particulate organic nitrates in the boreal forest area, likely in such relatively clean air regions. In boreal forest-urban mixed region, the organic nitrates mass loading was slightly higher due to higher NO_x concentrations originated mainly from the traffic sources. In addition temporal variety between the two measurement campaigns, boreal forest area measurements at early spring and boreal forest-urban mixed region measurements at autumn, may have influence on particulate chemical composition due to photochemical activity and other physico-chemical processes as well. In the present work, organic nitrates represented ON by estimation through separation into inorganic and organic forms of the functional group of NO_3 . In previous studies such as in Farmer et al., (2010), the estimation of ON was accomplished by using different analysis methods. The higher ON concentrations in Farmer et al. (2010) were due to distinct analysis methods and in addition, their measurements were conducted in polluted urban environments more conducive to ON formation.

The third objective was to assess how cloud processing affects the composition of organic-rich aerosol particles. Cloud droplet particles were mainly composed of LV-OOA and neutralized forms of sulfate and nitrate. Consistent with the long aging time in the air, cloud processing seemingly increased the aged low-volatile form of organics.

The fourth objective was to utilize PMF analysis to study the formation of organics, particularly PAHs, in the combustion process. In paper I, PMF analysis was, to the best of our knowledge, tested for the first time to study the composition of particulate organic aerosol in such direct combustion experiments. The PMF analysis method worked well in short-time resolution and sorting out the factors in a mathematically reliable manner. The five distinct factors identified established the complex character of organic aerosol in combustion emissions. The new HR PAH factor we identified yielded information about particulate PAHs, representing their time-dependent behavior in rapidly changing combustion conditions. This behavior is especially evident in the high formation of particulate PAHs under momentarily decreased combustion efficiency in smoldering combustion. Offline methods were unable to quantify this behavior.

While organic aerosol sources can be tracked well using the PMF analysis method from relatively long-term ambient data series and short experiments, sometimes mathematical criteria cannot resolve the occasional data peaks. Future data analyses could profit from paying attention to this feature. It may also be useful to add sulfate and other inorganic ions into the integrated organic and nitrate matrix for PMF analysis to study, for example, organic sulfates and to better understand submicron organic aerosol content in ambient air in real time.

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